MANUFACTURE OF SOAPS & RECOVERY OF GLYCERINE

BY

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THE MANUFACTURE OF SOAPS AND THE RECOVERY OF GLYCERINE.

A THESIS

Presented by

E. F. POLHMANN & H. W. MARTIN.

to the

PRESIDENT AND FACULTY

of

ARMOUR INSTITUTE OF TECHNOLOGY

For the Degree of

BACHELOR OF SCIENCE IN CHEMICAL ENGINEERING

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of Study in

CHEMICAL ENGINEERING.

1910. 22

Approved:

Harry McCormack
Professor of Chemical Engineering

H. M. Raymond
Dean of the Engineering Studies.

L. C. Morrison, Dean of Art Studies.

REFERENCES.

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Housebrandt.

Technology of Oils, Fats, and Waxes.
Lewkowitsch.

22124

THE MANUFACTURE OF SOAPS AND THE RECOVERY OF GLYCERINE.

THE MANUFACTURE OF BOARDS AND

THE RECOVERY OF FIBRE.

PART 1.

THE MANUFACTURE OF SOAP.

The first part of this thesis deals with the manufacture of soaps and the production of the waste liquor from which glycerine is recovered as a by-product, and this recovery is dealt with in part 11. Before describing our experimental work upon this subject we will discuss soaps in general, their properties, both chemical and physical, their source, formation, and the machinery necessary for their manufacture.

In its strict acception, a soap is the compound of an alkali, either potassium or sodium, with the higher fatty acids, especially with oleic($C_{18}H_{34}O_2$), palmitic ($C_{15}H_{31}COOH$), and stearic ($C_{17}H_{35}COOH$) acids. However, the insoluble compound of a fatty acid with a heavy metal is also termed a soap. For example, there is the lead soap or lead plaster of the pharmavy, iron and chromium soaps used in dyeing and in the printing of textiles, alumina soap used as a thickner of lubricating oils, and many other such. Potassium or potash soaps are usually soft, and are known as soft soaps, while sodium or soda soaps are hard and come into the market under the name of compact, cut , or filled soaps.

Commonly considered, soap is, according to its quality and the use for which it is intended, a

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mechanical mixture of the above mentioned compounds, with varying proportions of water, with soluble alkali compounds of the rosin acids, with sal soda, with sodium silicate or soluble glass, or with other inert, detersive, or odoriferous agents, incorporated for the purpose of cheapening the product, improving its appearance, increasing its detersive action, or overcoming its natural odor with an agreeable perfume. Among the adulterants benefiting or harming a soap, are, ochre, ultramarine, sodium aluminate, borax, gelatine, resin, vermillion, copper arsenite, alcohol, vaseline, tar, sugar, champhor, petroleum, phenol, naphthalene, bran, starch, etc. Therefore, commercial soap is a mixture of pure soap with a dilutent, as water, with body imparting substances, as talc, starch, or petroleum residue; or with detersive agents in aqueous solution/ as sodium carbonate, borax, or sodium silicate. These additions may all be present in a single soap but the nature and amounts of the addition present depends upon the character of the soap itself and the purpose for which it is intended.

Soaps may be divided into three general classes viz.- laundry or household soaps, generally containing an excess of alkalies in the form of either sodium carbonate or sodium silicate, or free alkali, and resin; toilet or medicated soaps, the best grades of which are free from impurities and free alkali, or contain

medicinal agents; and commercial soaps, also termed industrial soaps, which may be subdivided into (a) soft soaps, and (b) hydrated or hard soaps, as has already been mentioned.

The common fats and oils contain the fatty acids in combination with glycerine, termed glycerides, and it is from these that soaps are generally made. Saponification is the term applied to the process of decomposing the glycerides and forming a soap, and this can be effected in the following ways:-

Aqueous Saponification. This is the most simple and convenient method for the hydrolysis of the glycerides except when alkalies are used for the saponification. The operation may be expressed by the equation: $C_3H_5(C_{18}H_{35}O_2) + 2H_2O = C_3H_5(OH)_3 + 3C_{18}H_{36}O_2$, the mixture being subjected to the action of water or steam at high temperatures or pressures. If the water is acidulated with a dilute mineral acid, the hydrolysis may be accomplished at a much lower temperature, for the acid serves as a catalyzer and accelerates the reaction between the water and the glycerides of the fat. This method is employed chiefly for the manufacture of candle stock, and the preparation of glycerine.

(2) By the action of lime, termed lime saponification. This method may be illustrated by the equation: $2C_3H_5(C_{18}H_{35}O_2)_3 + 3CaO + 3H_2O = 3Ca(C_{18}H_{36}O_2)_3 + 2C_3H_5(OH)_3$. The stock, usually tallow, is melted and

then run into the digester together with the lime that has been previously thoroughly mixed with water. The quantity of unslacked lime commonly used for the saponification is from 2 to 4 percent of the weight of the tallow, for, although 8.7 percent is theoretically required, the above amount has been found to be sufficient in practice. The charge, having been added, the digester is closed and the steam turned on, and maintained at a pressure of from 8 to 10 atmospheres for a period of from 4 to 10 hours, or until saponification is complete, whereupon, the contents of the digester are blown into wooden tanks. After a time the mass resolves itself into two layers, the supernatant lime "rock" consisting of lime soap and fatty acids, and the "sweet" water, in which is dissolved the glycerine, liberated as shown in the above equation. This glycerine solution is allowed to flow to the glycerine plant where it is treated as described in part 11.

93- Acid Saponification. The melted raw material is run into a lead lined tank and treated with 4 to 12 percent of concentrated sulphuric acid, and the mixture is subjected to the action of superheated steam. After the acidification the liquor is removed and the fatty acids washed free from all traces of the acid. The following equation illustrates the process:-

$C_3H_5(C_{18}H_{35}O_2)_3 + H_2SO_4 = C_3H_5(SO_3OH) + 3(C_{18}H_{36}O_2)$.

94- By the action of caustic alkalies:-

$C_3H_5(C_{18}H_{35}O_2)_3 + 3NaOH = C_3H_5(OH)_3 + 3C_{18}H_{35}O_2.Na$. This equation represents the reaction employed in ordinary soap making, and will be treated more in detail farther on. The caustic unites with the fatty acid radical to form the soap, and the glycerine is formed as a by-product which is recovered from the waste soap liquor.

The first three of these methods are used mainly for the production of fatty acids, the last for soap making. In a general way these four methods illustrate the methods of the formation of a soap and the chemistry envolved. If the tallow is choosen as the raw material, the yield of solid fatty acids by the lime saponification is from 44 to 48 percent; while the aqueous saponification admits of a slightly higher yield, that is, about 50 percent. Acid saponification yields upwards of 55 percent of fatty acids, and alkali saponification yields about 50 percent. With lime saponification practically all of the glycerine, upwards of 10 percent, is obtained, and the same may be said for the alkali saponification; while with the acid saponification not more than 3 percent is recovered.

" The chemistry of saponification was first explained by Chevreul, who attributed the cleansing action of soap to the free alkali formed by the decomposition of the soap when brought into solution. Krafft and Stern confirm this, and hold that in the hot dilute soap solution, part of the soap is dissociated into

free acid and free alkali, but on cooling, the free acid unites with some of the undissociated neutral soap, to form insoluble bi-palmate, bi-stearate, or other bi-salt, leaving the free alkali in solution. The turbid appearance of the solution may be due to oily drops of the free fatty acids."

Amonge the raw materials used for the manufacture of soaps are: tallow, grease, and bone stock. These classes may occur in various grades, and in determining the quality, buyers as a rule, depend on the simple tests of color, odor, and grain, supplemented by the titer or hardness test, the percentage of moisture, melting point, and the percentage of free fatty acids. The raw materials are not necessarily of animal stock as described above, but may be of vegetable origin, as cotton-seed oil, coconut oil, palm oil, palm-kernel oil, corn oil, olive oil, red oil, etc., and in their many modifications.

In the preceeding discussion of the raw materials used in soap manufactures, we have considered those bodies which carry two compounds, viz., a glyceride and a caustic alkali, which, when in chemical combination, form a soap. Therefore, soap boiling consists essentially in bringing a fatty body and a caustic alkali in aqueous solution in contact under suitable conditions, whereby a simple chemical reaction ensues

with the formation of an alkaline salt of a fatty acid and the liberation of glycerine. The chemical properties of the various glycerides which constitute the various fats and oils employed in soap manufacture determine their behavior in the soap kettle and the variation in the amount of alkali absorbed by any particular fat or oil is due to the difference in the composition of the glycerides themselves and from the varying proportions in which the glycerides occur in any particular stock. As the molecular weight of the glyceride increases the amount of alkali necessary for saturation decreases, hence, those commercial fats and oils in which the glycerides of low molecular weight occur possess the highest alkali absorption in proportion to their weight. The greater quantity of salt required for graining the soap made from such stock is due to the presence of those glycerides of low molecular weight whose greater solubility in brine of the sodium salt is a marked characteristic. As the glycerides increase in molecular weight, the solubility in brine of the soap obtained therefrom diminishes, hence, less salt is required for graining.

The manner of effecting the combination or chemical reaction between a fatty body and a caustic alkali and the conditions under which the reaction is completed gives rise to three general classes of soap manufacturing processes, viz.- boiled, semi-boiled, and cold process, whereby soap, to which the same des-

criptive terms may be applied as well, are produced. This classification is arbitrary and is not based on any essential chemical differences in the processes. The division is more mechanical than chemical and has reference chiefly to the time required, the artifical heat employed, andthe mechanical apparatus necessary to a satisfactory operation of the process.

A cold soap is one made by the direct combination of the materials in the proportion in which they are to remain in the finished soap, the combination being effected without the aid of heat other than that required to bring the ingredients to the requisite temperature and that heat evolved by the chemical reaction.

Boiled soaps, also called settled soaps, are those which in the process of manufacture have been subjected to changes whereby the soap is purified and the glycerine separated.

A semi-boiled or run soap, is one containing all the materials added to the kettle but has not been subjected to the graining process.

The manufacture of a settled soap is accomplished in the following steps: (1) saponification; (2) graining and settling; (3) crutching; (4) framing; (5) slabbing; and (6) drying, pressing, etc. These soaps

are the most important and constitute the class most generally manufactured and used. All household soaps are made by this process as well as the base for toilet soaps, and it is this class of soaps that we produced in the laboratory.

Three stages are required for the complete formation of glycerine and the combination of the alkali with the fatty acids, by the saponification of the glyceride stock, and each stage manifests itself in certain characteristic conditions, viz.- the emulsion formed on admixture of the stock and lye, the pasty mass obtained on continued boiling, and lastly, the final condition resulting from boiling the pasty mass with an amount of alkali sufficient for complete saponification. These three successive stages of saponification may be represented by the chemical formulas:
Raw Materials:

Stearin (tallow) $C_3H_5(C_{18}H_{35}O_2)_3$ Caustic soda:$3NaOH$

1. Emulsion $C_3H_5OH(C_{18}H_{35}O_2)_2$ Soap: $C_{18}H_{35}O.NaO$
   Caustic soda: $2NaOH$
2. Pasty mass $C_3H_5(OH)_2(C_{18}H_{35}O_2)$ Soap: $2C_{18}H_{35}O.NaO$
   Caustic soda: $NaOH$
3. Glycerine $C_3H_5(OH)_3$ Soap: $3C_{18}H_{35}O.NaO$

Graining. The purpose of graining is to separate the soap from the superfluous water with which it is associated, and which, forming the menstrum for

for the salt, glycerine, lye, impurities in the stock, etc., constitutes the soap lye. The salt is added either as the dry salt or as a saturated brine, in small quantities at a time, to the quietly boiling contents of the kettle and thoroughly boiled with it until a portion taken on a paddle coagulates or separates so that waste lye runs from it. The waste lye should be clear, of a salty taste, and should not contain free alkali in excess of 0.4 percent. This amount of free alkali in waste soap lye is not perceptible to the taste. The more concentrated the salt solution in contact with the soap the less water will be retained by it. In boiling this character of a soap the stock lye should not have a greater density than 13 degrees Baume', and should contain from 7 to 10 percent of salt. This is the lowest density that will remove the soap completely from solution, while the stock lye is the clearest and least discolored, and is the most valuable, owing to the high percentage of glycerine present. When the desired grain has been obtained the soap is boiled up to the top of the kettle, the steam turned off, and the contents allowed to rest until the following morning.

Settling. Fitting or settling the soap is the term applied when weak lye or water is added to the soap to

thin it to the desired consistency. The strengthening lye from the preceeding change is withdrawn and the soap boiled up with live steam to the top of the kettle and it is then allowed to stand for five days, during which time the contents of the kettle, because of the different specific gravities, resolve themselves roughly into two portions, viz.- the finished soap carrying about 30 percent of water, and the niger, which carries considerably more water than does the supernatant soap, as well as the impurities and coloring matter settled from it. The niger constitutes from 20 to 25 per cent of the volume of the settled soap in the kettle.

The detergency of soap is greatly increased by the addition of certain substances called fillers, in aqueous solution, while the soap is still in the fluid condition. The substances used as fillers have already been mentioned, and the nature and amount of the filler determines whether the soap is heavily or lightly filled.

Crutching. For the incorporation of the filling material into soap, the belt driven crutcher is generally employed. There are three types of this machine each possessing their several points of excellence, but we will attempt to describe only one of them. This

consists of a cylindrical vessel in which is mounted a vertical shaft carrying a series of horizontal paddles which rotate entirely within the body of the soap, which remains practically stationary. With this type it is impossible to incorporate air into the mass of the soap as the mixing is done entirely within the body of the soap. The capacity of the crutcher is about 1200 pounds. The liquid soap is transferred to the crutcher by means of a pump, generally of the Tabor, Hersey, or Johnson rotary type.

Framing. The soap frame consists essentially of an uncovered box having a capacity of about 1200 pounds and supplied with removeable sheet-steel sides, and ends of wood or sheet steel set on a wooden bottom, which is mounted on truck wheels. The soap from the crutcher is emptied into the frame and allowed to remain there until it has hardened, whereupon the sides are removed and the soap allowed to rest on the bottom for several weeks or until the soap has cured, that is, until it has dried. This operation requires a great deal of floor space and is objectional for that reason, and although this method of curing has so many disadvantages it is still used almost entirely by soap manufactururers. A better method, and the one used by the more up to date plants is the following: The liquid

soap is run to the upper story of the building into a large vat or tank. From this tank it flows by gravity over a system of steam heated rollers, seven in number, and each a little closer than the preceeding one. The soap is spread over the roller in a thin layer or film, from which it is taken by the next roller and so on, until it reaches the last, from which it is removed by means of a scraper which breaks it up into thin strips or shavings. These shavings fall onto a belt moving very slowly and which enters a dryer, which is simply a wooden box about 10 feet high, 8 feet long, and 5 feet wide, supplied with glass windows by means of which the interior can be seen. This dryer is supplied with steam pipes, and as the soap travels back and forth on the belt within it it is dried and cured. The whole process requires about an hour. The shavings leaving the dryer fall into a basket, which when full, is carried to the press, and the chips pressed into large slabs, similiar to those coming from the frames.

Slabbing. The slabber is a machine for cutting the slab of soap into smaller slabs, and consists of a frame work having a series of horizontal parallel wires at a distance apart corresponding to the width or height of the unpressed bars of soap. The slab of soap mounted on a truck is pushed along under the frame of the

slabber and as the soap comes into it it meets the taut steel wires and is cut into smaller slabs. These slabs are then removed to the cutting table, where each is cut into bars.

Each slab is lifted onto the cutting table and pushed lenghtwise through one or two wires held in the cutting head, by means of which, it is cut into two or more narrower slabs as wide as the single bar is long. These slabs are then cut at right angles by another attendant to the dimensions corresponding to the width and thickness of a single bar. The individual bars are then slightly separated from one another so that the air may circulate freely around them. When the truck is full of these bars it is removed to the drying room.

The purpose of the drying room is to hasten the evaporation of the water from the surface of the bar so that there may be formed a thin crust of comparatively hard soap which serves to retard further evaporation from the interior of the bar, and which allows the bar to be pressed and stamped without the soap adhering to the dies. Now there is an unequal equilibrium of moisture content between the exterior and interior parts of the bar, a partial explanation of the

similar as to the long rounds used if it were the
leaf shaped views and in fact long-smaller slides. Short
slides are then required to the existing tools, where
exact is not into here.

Each slab is fitted onto the rotating table
and passed lengthwise through one or two stone beds in
the cutting head, by means of which, it is cut into
two or more narrower slabs the size of the blocks that
is used. These slabs are then cut at right angles by
another attachment to the stone-cutting corresponding to
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lows the water in the pressed out chamber to come
accretion to the slab. The change is so successful
ful of adjusting between the material and in-
terior parts of the bar, a partial application of the

sweating to which soaps are universally susceptible. This accumulation of moisture does not develop until after the bar is wrapped and packed. With the soap wrapped and packed in a box the conditions are naturally different. The tendency for the moisture to pass from the interior of the bar to the drier surface remains, but further evaporation from the exterior of the bar is checked. Here the moisture accumulates and softens the soap, which in turn adheres to the wrapper. The drying room is either furnished with ventilating fans or steam or cold air pipes, or both. The requirements for the drying room are that a large volume of air must be furnished at the required temperature and be maintained in rapid circulation. A temperature of 80 to 100 degrees F. is productive of the best results.

When the soap comes from the drying room it is ready for pressing. This consists in pressing the cakes of soap into the desired shape and volume, and stamping them with the trade marks etc. The automatic steam-power soap press is the one universally used at the present time and they have a guaranteed capacity of from 60,000 to 75,000 cakes per day of 10 hours.

The semi-boiled soap as has already been mentioned is primarily a cheap method of soap manufacture, with economy in fuel, labor, and time. It is best,

however, to give the soap a simple purification by graining it sharply, thus prolonging the time consumed in its manufacture by one day. The process in outline is similiar to that just described, and is the method used exclusively for the manufacture of soft soaps.

The production of soap by the cold process far surpasses all other methods in the economy of every element entering into the cost of production, but it possesses certain paramount disadvantages, which restrict its use to a very limited field. The mechanical equipment required consists simply of tanks containing the fat, oil, and caustic lye, a crutcher in which the ingredients are mixed, and frames to receive the mixture and in which the chemical reaction of saponification continues, if under favorable conditions, to completion. Although this process varies in most of its details from the manufacture of laundry soaps as we have already described, we shall not attempt to go farther into the discussion of this method, nor shall we give in greater detail the method we have just described, concerning the various modifications, alterations, etc., which the different manufactururers use, for we have covered briefly all the essential points to be observed in the production of a soap in our general outline of their manufacture.

The method employed in the making of a soap by us in the laboratories of Armour Institute Of Technology was exactly similiar to that which we have outlined under the heading, the manufacture of boiled orsettled soaps, with the exception that our apparatus was crude, on a smaller scale, and that we added cotton-seed oil when the saponification had reached the pasty state.

Trirty five pounds of tallow, having a saponification number of 195, was placed in a kettle and melted by means of a steam coil placed in the bottom thereof. When the tallow was in the liquid condition we added 20 pounds of our caustic alkali solution containing 6 percent of NaOH and then boiled the mixture. After about 10 hours boiling the emulsion stage was completed, that is, the first third of the alkali was then in combination with the tallow (stearin). At the end of the next 15 hours boiling we judged that the pasty state was completed, that is, two-thirds of the caustic was in combination with the stearin, and at this point we added 15 pounds of cotton-seed oil having a saponification number of 137, and 20 pounds more of the lye. The boiling was then continued for another period of six hours, whereupon the saponification was complete, that is, all the alkali was in combination with the s

stearin, for the solution on top boiled very quietly, was frothy and smooth, and the stock would slide from the paddle in large transparent flakes, and when a small portion was rubbed between the fingers it curled up smooth and dry, without any indication of grease.

The saponification being complete, the stock was ready for the graining. While the mixture was boiling quietly we added a little salt, NaCl, but this small addition soon threw so much soap out of solution that our kettle would not hold it. To overcome this difficulty we removed all the soap from the kettle and made up a brine solution which we heated to boiling in the kettle and then added a little of our soap solution and continued the boiling until it was all thrown out of solution, whereupon we allowed it to settle and solidify, and then removed it, leaving the brine in the kettle for the next lot, adding a little salt each time to make up for that used. Our kettle being small, as the soap was thrown out of solution and solidified, it filled the entire kettle, so that it held a large proportion of water mechanically, because of its expansion. So when the soap came from the kettle it was extremely soft and contained 80 percent of water. The entire lot of soap having been treated in this way weighed 190 pounds, which calculated to a 30 percent

moisture basis, that being the average moisture content of such a soap, made the yield 50 pounds of soap, or 51 percent of the raw materials used.

Because of the small size of our kettles and the expansion of the soap when thrown out of solution quite a quantity of the waste soap liquor was taken up mechanically, so that we did not attempt to measure this part, but we had to eliminate it from the soap. To do this we made up a brine solution and washed the soap with it, so that it finally contained very little free alkali as will be seen from the analysis which concludes part 1 of this thesis. Now the mass of soap was a soft slimy mixture and it had to be dried, but because it contained so much water it was impossible to use the temperature of boiling water (100 degrees C.) because the water being in such excess of the soap formed a fluid which ran through the containing vessel, so we had to resort to air drying. As the soap became dryer we cut it up into small pieces and spread them out on screens. When it became dry and hard we pressed them together into cakes.

It was very difficult for us to find a good method for analyzing soaps, for each text book and soap chemist advised a different method, and we could not get good checks on our analysis, that is, checks that

satisfied us. However, we finally came across a satisfactory method given in bulletin 109, of the United States Agricultural Department, which we used except for a slight modification which we introduced.

As we have already mentioned the moisture content of the outer layer of a bar of soap may be very different from that of the interior of the cake. We took a portion of each lot of soap, mixed it, and pressed it into a cake, and after allowing it to cure for some time, we cut it in two in a diagolal direction and cut from one of these fresh surfaces, in thin layers, a sufficient quantity for all determinations, taking care to cut entirely across so as to get a fair sample and proportion of the outer and inner portions.

Moisture. Heat two grams of the finely shaved soap for two hours in an oven at 105 degrees cantigrade. The loss is considered as water, though of course, this is not accurate, as volatile oils may constitute a part of the loss, and on the other hand, all water may not be driven off, and if the soap contains free alkali carbon dioxide may be absorbed from the air.

Insoluble Matter. Dissolve 5 grams of soap in hot water (use about 75 c.c.). Filter on a Gooch or weighed paper and wash with hot water; dry at 105

degrees C., weigh, and calculate the percentage of mineral matter.

Total Fatty Matter. To the filtarte from the insoluble matter add 40 c.c. of half-normal sulphuric acid, heat on the water bath until the fatty acids have collected in a thin layer on top, cool in ice water then heat again with water, cool, remove fatty layer, wash with ice water, dry with filter paper, unite the acid liquids, transfer to a separatory funnel, and shake out with two portions of 50 c.c. each of gasoline, wash the gasoline twice with 20 c.c. of water. Evaporate off the gasoline, add the cake of fatty acids, etc., dry at 100 degrees centigrade and weigh as total fatty matter.

Total Alkali. Heat the acid liquid from the determination of total fatty matter to drive off traces of gasoline, cool, add methyl orange, and titrate the excess of acid with a half-normal NaOH solution. From this titration calculate the amount of acid neutralized by the alkali in the soap and figure to percentage of sodium monoxide. A more rapid method is to ash the soap, dissolve the ash in water, and titrate.

Free Alkali. Treat the freshly cut surface of the soap with a few drops of phenolphthalein; if it does not turn red it may be assumed that free caustic

alkali is absent. If free alkali is present, dissolve two grams of the soap in 100 c.c. of neutral alcohol, filter from the undissolved sodium carbonate etc., wash with alcohol, add phenolphthalein, titrate with standard acid, and calculate to percentage of free alkali as NaOH. Should the alcoholic solution be acid instead of alkaline, titrate with standard alkali and calculate the percentage of free fatty acids as oleic acid. Wash the portion insoluble in alcohol with water add methyl orange to the washings, and titrate with half-normal sulphuric acid. Calculate to percentage of sodium monoxide present as the carbonate, or possibly as the borate or silicate. If borax is present boil off the CO_2 after neutralizing exactly to methyl orange; cool, add mannite and phenolphthalein, and titrate the boric acid with standard alkali.

Unsaponified Matter. Dissolve 5 grams of soap in 50 c.c. of 50 percent alcohol; if any free fatty acids are present add just enough standard alkali to neutralize them and wash into a separatory funnel with 50 percent alcohol. Extract with 100 c.c. of gasoline (B.P. 50-60 degrees). Wash the gasoline with water, evaporate, and weigh as unsaponified matter. This may consist of fat that has not been converted into soap or of hydrocarbons.

Glycerine. Dissolve 20 to 25 grams of soap in hot water, add a slight excess of sulphuric acid, and heat on the water bath until the fatty acids separate in a clear layer. Remove the fatty acids and filter the acid solution into a graduated flask. Remove the chlorides and the soluble fatty acids by adding crystals of silver sulphate, cool, make up to mark, mix, allow to settle, filter through dry paper, take an aliquot portion corresponding to five grams of soap, and determine the amount of glycerine by Hehner's bichromate method, as described in part 11. This mathod cannot be used when sugar is present as it also would reduce the bichromate.

Soap.	Ivory.	Ours.	American F.
Moisture.	18.25	29.92	16.98
Dry Basis.			
Total Alkali Na_2O	9.23	9.86	9.50
Free Alkali NaOH	1.48	1.59	1.21
Na_2O as Na_2CO_3	0.42	0.00	0.36
Total Fatty Matter	87.64	86.92	87.57
Unsaponified "	1.22	1.63	1.36
Glycerine	0.00	0.00	trace

Soap.	Varg.	Ours.	American T.
Moisture.	18.38	20.02	16.98
Dry Basis.			
Total Alkali Meqo	0.32	0.80	0.80
Free Alkali Meqo	1.48	1.80	1.21
Acid as Meqo/g	0.45	0.00	0.30
Total Fatty Matter	87.44	84.82	87.27
Unsaponified "	1.32	1.82	1.44
Glycerine	0.00	0.00	trace

DESIGNED TO WITHSTAND A 27 INCH VACUUM

DETAIL OF STILL
FOR
GLYCERINE RECOVERY
ARMOUR INSTITUTE OF TECHNOLOGY
SCALE 6"=1' DEC. 1923
H.W. HAYEIM
E.E.C. PALMER

E. F. Fohlmann '10 H. W. Martin '10.

Letter. Name. List of Materials.

A. Still Body of ⅛" spun copper with 1" flange with 20-$\frac{3}{32}$" holes.
1 brazed saddle flange with tapped hole for ¼" brass pipe.
2 " " " " " " " " ¾" " " .
2 " " " " " " " " ⅜" " " .
1 " " " " " " " " ½" " " .
1 cast brassing, 8½" outside dia. and 6½" inside dia. with 20-$\frac{9}{32}$" holes.
Coil of ⅜" copper condenser tubing, 5 turns, 5" dia., ends fitted with brass reducing couplings.
3" gauge glass with cock.
2 brass lugs, ⅜" thick, ⅛" equal legs to be brazed on body of still.
[illegible] gauge and thermometer (0-300° C).
1 perforated superheated steam coil, 50-¼" dia. holes.
1 cap for ¾" pipe
Cover of ¼" cast brass, having 1-⅜" high, ¼" dia., pipe-tapped projection, and 1-⅜" high, ½" dia projection; also a ½" boss with 1¼" pipe-tapped hole, also 1" flange with 20-$\frac{9}{32}$" holes.

B. Catch-all. Cover, ¼" cast brass, having a ½" boss with 1¼" pipe-tapped hole. Cover tapped to screw on 4" body.
Body of 4" brass tubing, ⅛" thick, threaded at top to receive cover.
1 brazed saddle flange with tapped hole for 1¼" brass pipe.
1 " " " " " " " ½" " " .

C. Superheater 2 covers, ¼" cast brass, tapped to screw on 4" body.
½" boss with 1¼" pipe-tapped hole.
Body of 4" brass tubing, 7" long.
1 brazed saddle flange with tapped hole for ½" brass pipe.
2 " " " " " " " " 1¼" " " .
12-$\frac{5}{8}$" dia, 6¼" long copper condenser tubes, bushed to a copper plate ⅛" thick which is brazed to interior of 4" tube.

E.F. Pohlmann '10. H.W. Martin '10.

Letter Name. List of Materials.

D. Condenser. 2 covers, each of ¼" cast brass, and tapped to screw on 4" body; bottom one has ⅜" boss with ½" pipe-tapped hole.

Body of 4" brass tubing, ⅛" thick.

2 brazed saddle flanges with tapped hole for 1¼" brass pipe.

2 " " " " " " ¼" copper " .

Coil of ¼" copper condenser tubing, 4 turns, 3" dia., ends fitted with brass couplings connected by ¼" exterior pipe, 5" long elbows with ⅛" water inlet and outlet pipes.

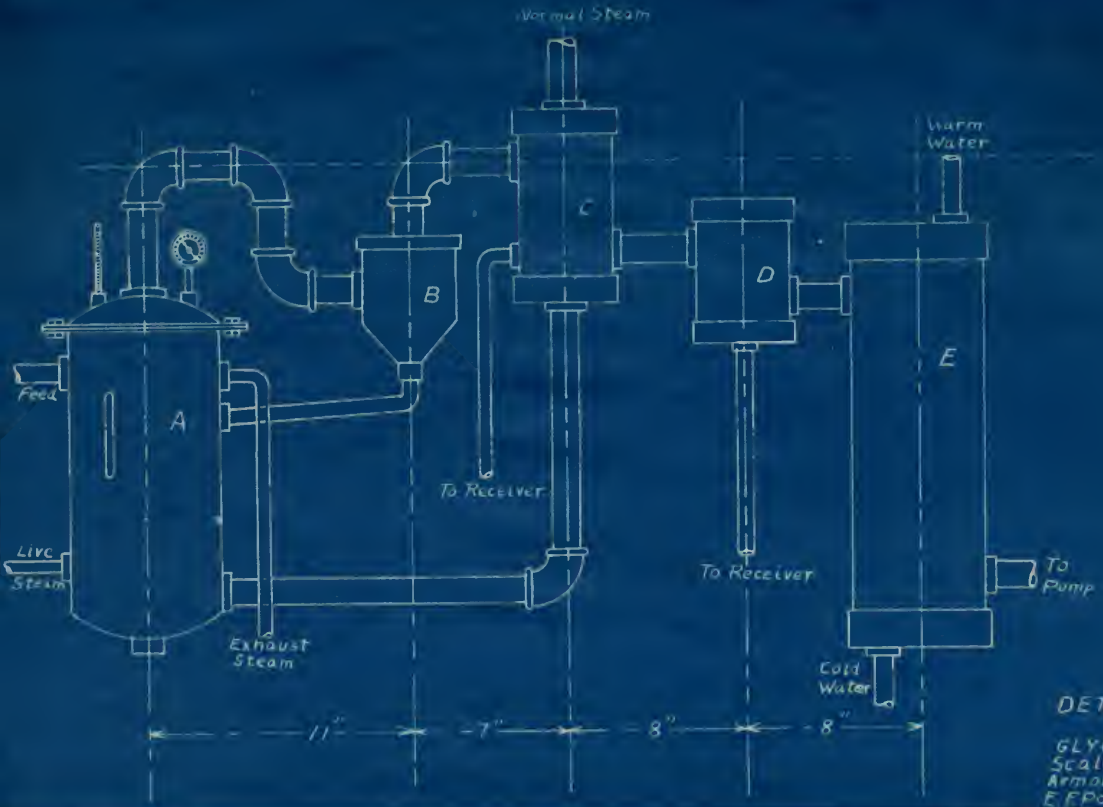
E Sweetwater

Condenser. 2 covers, each of ¼" cast brass, and tapped to screw on 5" body. One has a ½" boss with ½" pipe-tapped hole; other has a ½" boss with ¾" pipe-tapped hole.

Body of 5 brass tubing, 16" long.

2 brazed saddle flanges with tapped hole for 1¼" brass pipe.

9- ¾" dia., 14" long copper condenser tubes bushed to a copper plate ⅛" thick which is brazed to interior of 5" tube.



DETAIL OF STILL
for
GLYCERINE RECOVERY
Scale 2"=1' Feb. 1910
Armour Institute Technology
E.F. Pohlmann H.W. Martin

PART 11.

THE RECOVERY OF GLYCERINE.

In the discussion of the manufacture of settled soaps in part 1, we traced the progress of a boil of soap with the formation of the various lyes. These lyes contain all the glycerine which the natural oils and fats are capable of yielding, and may contain as much as five to eight percent of pure glycerine; but usually the percentage is lower, about three percent. Besides this, the lyes contain varying amounts of common salt, sodium hydroxide, sodium carbonate, and sodium sulphate, contaminated by more or less soap in suspension, and soma mucilaginous matter or animal tissue remaining with the stock when rendered. This often foul-smelling liquor, a by-product with the soap maker, now becomes the raw material of the glycerine refiner.

The specific gravity ofthe waste soap liquor varies from 1.07 to 1.14 according to the amount of sodium chloride in solution. Since, in the recovery of glycerine, the impurities must all be gotten rid of, the value of the lyes depends on the percentage of glycerine and on the freedom from free sodium hydroxide and sodium carbonate.

PART II.

THE MANUFACTURE OF CEMENTITE.

In the discussion of the manufacture of cementite soaps in part I, we traced the pretreatment of a boiling soap into the formation of the various lime soaps and fats are capable of yielding, and may contain as much as five to eight percent of pure glycerine; but usually the percentage is lower, about three percent. Besides this, the lime soaps contain varying amounts of combined water, sodium hydroxide, sodium carbonate, and combustible matter, consisting of more or less soap or lime soap in emulsion, and some unsaponifiable matter or animal charge remaining with the stock when rendered. This latter consists principally of, a by-product with the hydrocarbon nature, and some unsaponifiable matter or animal charge remaining with the stock when rendered. This often called "oxidized tallow", and becomes the raw material of the hydrocarbon industry.

The specific gravity of these soaps ranges from 1.07 to 1.14 according to the amount of glycerine, the temperature when, time, in the receipt of glycerine, the temperature must all be taken into the saponification. Time, in the receipt of glycerine, the temperature must all be taken into the saponification. Time, in the receipt of glycerine, the temperature must all be taken into the saponification.

One method of purifying the lyes is the purification by the removal of the fatty acids, rosin acids, and other organic impurities. The liquor then contains the pure glycerol and salt in solution. The latter is removed by heating the liquor to the "salting-point" in fire heated vessels or tube heated evaporators. The "salting-point" is reached when the liquid has acquired the specific gravity of fourty-four degrees Twaddell at fifteen degrees Centigrade. If the evaporation is carried on farther, salt will be deposited, while the specific gravity and percentage of glycerol will rise. Consequently, the vessels in which the evaporation is carried on beyond the salting point must be provided with stirring and scraping arrangements to re-the salt as it separates, since all tube evaporators are liable to incrustation with salt and the gradual stopping up of the heating tubes. The finished crude glycerine which comes from the evaporator has a specific gravity of about 1.3, and contains about eighty percent of glycerole, ten percent of salt, and the remainder of water and small amounts of impurities. The methods of purification do not differ much, hence, the method taken up in detail farther on is sufficient to illustrate the general plan of procedure during purification and concentration.

It might be said here that crude soap-lye glycerine containing a considerable quantity of thio-sulphates, sulphides, and sulphites, are almost valueless to the refiner of crude glycerine.

There are many different systems of apparatus used for the recovery of glycerine from the waste soap liquor, and before going into our experimental work upon this subject and the design of our plant, which is given in detail in the accompanying blueprints, we will describe the method and apparatus used by Armour and Company.

The waste liquor from the soap works, which has a specific gravity of 16.5 degrees Baume' and contains 3.5 percent of glycerine, and 0.5 percent of sodium chloride, is run , by means of pipes, to the waste lye tanks, situated in the upper story of the works. These tanks are lead lined, nine feet long, six feet wide, and twelve feet deep. Here 60 degree Baume' sulphuric acid is added until the liquor is neutral. The mixture is then agitated by means of compressed air entering through pipes at the bottom, and the albuminous matter precipitated by the addition of aluminium sulphate, although basic sulphate of iron may be used.

The liquor is then passed through a filter press, employing eight-duck canvas as the filtering

medium, under a pressure of 45 pounds per square inch. The precipitate is useless and is sent to the dump. The filtrate is run into another tank which is 15 feet wide, 50 feet long, and 14 feet high, and is now somewhat acid. In this tank enough caustic soda is added to neutralize the acid, and the liquor is then run into another tank, about the same size as the one just described, where it is stored until desired for further treatment.

The next step is the evaporation of the liquor andthis is done in a triple effect evaporator. In each effect are steam coils and the steam enters the first at a pressure of 75 pounds per square inch, and leaves the last at a pressure of 15 pounds per square inch, thus passing through the whole three effects. The first effect is maintained at a vacuum of five inches of mercury and the lye enters it at 15 degrees Be'. and leaves it at 18 degrees Baume'. From here it passes to filter box which is six feet long, four feet high, and four feet wide, holding a 36 mesh screen, and maintained at the same vacuum as the first effect, that is, five inches of mercury. This vacuum sucks the liquid through the screen, andthe salt is retained by it. The filtrate is then run into the second effect which is kept at a vacuum of 15 inches and where it is con-

centrated to 22.5 to 23 degrees Baume'. It is again run to a filtering box exactly similiar to the first one, with the exception that it is maintained at a vacuum of 15 inches of mercury. From here the liquid, at 23 degrees Baume', is sent to the third and last effect, where it is concentrated to a specific gravity of 34 degrees Baume' and again filtered free from the salt as before, the vacuum in thisicase being the same as that of the last effect, viz.- 26 inches of mercury. The vapors from all three effects pass through condensers on the roof of the plant, where they are condensed and run to the sewer.

When the liquid leaves the last evaporator, all the water has been removed from it and it is two-tenths of one percent alkaline. Enough 74 percent NaOH is then added to it to make its alkalinity five-tenths of one percent which is done in a tank, and after it has been so treated it is ready for the distillation.

It is, therefore, run into the glycerine still which is an asbestos covered cast iron cylinder, nine feet high and four feet in diameter, and contains a one-inch copper coil through which steam, at 40 pounds pressure, is passed. The steam enters at the top of the still through a one-inch pipe, and also leaves it at the top through the same sized pipe which leads to a

coil in the superheater. The crude glycerine enters the still through a two-inch line at the top and enough of it is allowed to flow in to keep the still about three fourths full. The still is maintained at a vacuum of 27 inches of mercury. The glycerine vapors pass off through an 18-inch goose-neck to the superheater. From here they pass to two receivers, each eight and one half feet high, and three and a half feet in diameter, which are arranged in a line with the still. The heavier vapors fall into the first receiver, while the lighter ones fall into the second, which is the farther from the still. Neither of these receivers is under a direct vacuum.

The vapors which do not condense in either one of the receivers pass to a third vessel, from where, the so called "sweet-water" is pumped to the superheater, giving up some of its heat. The liquid in the first receiver has a specific gravity of 22.5 degrees Baume', while that in the second receiver is about 16 degrees Baume'. The still contains 180 pounds of glycerine to an inch in height, thus having a capacity of about 15,000 pounds of the crude liquid. The glycerine in the second receiver is either put back into the still, or stored until there is a large amount on hand, in which case it is evaporated down to 29

degrees Baume' in another still under a vacuum of 25 inches of mercury, and a steam pressure of 15 pounds per square inch, and sold as P.Y. (pale yellow) glycerine.

The glycerine from the first receiver is run into a tank and purified by dilution with water to a specific gravity of 15 degrees Baume'. To every thousand pounds of this liquid is added one-quarter of a pound of 66 degree Baume' sulphuric acid and an equal amount of 74 percent sodium hydroxide to neutralize the acid, and 20 pounds of bone black to bleach the glycerine. The whole is then agitated by means of compressed air, run through the filter press at a pressure of 45 pounds per square inch, neutralized with soda ash, one pound in excess, and again filtered as before to remove the soda. The glycerine is then fed to a concentrator under a 25 inch vacuum, where it is evaporated down to 29.75 degrees Baume'. It is then fed for a second distillation under the same conditions as before. Each still has a separate pump, andthe action is the same throughout with the exception that theglycerine now has a strength of 30.5 degrees Baume', and the second receiver contains steam coils to concentrate the glycerine therein to the same gravity as that in the first receiver. It then goes to a tank for bleaching, for which

purpose 25 pounds of bone-black are added to every thousand pounds of the glycerine. It is then filtered and sent to the storage tanks ready for shipment. The P.Y. glycerine is bleached by adding eight pounds of bone black to every thousand pounds of the liquid.

Hence, there are two products of the plant, the P.Y., or commercial glycerine, and the C.P. or glycerine used for medicinal purposes. Pure glycerine is a colorless, oily liquid, having a sweet taste, and miscible in all proportions with water and alcohol, but insoluble in ether. When cooled to a low temperature glycerine solidifies, but the crystals thus formed do not melt below 17 degrees Centigrade. It boils at 290 degrees, and has a specific gravity of 1.265 at 15 degrees Centigrade.

The waste lye which we used in our experimental work, came from the soap works of Armour and Company, in a large galvanized iron cylindrical tank containing about 100 gallons. The following teste were made on it:

(1) Specific Gravity.

(2) Total Alkali as Sodium Hydrate.

(3) Free Alkali as sodium Hydrate.

(4) Combined Alkali as Sodium Carbonate.

(5) Sodium Chloride.

(6) Glycerine.

The method of analysis was as follows:

Specific Gravity. Determined by means of the Westphal balance.

Total Alkali as Sodium Hydrate. Ten c.c. of the waste lye, filtered free from suspended impurities, was placed in a beaker and diluted to about 150 c.c. with distilled water. A few drops of methyl orange was then added and titrated with half-normal sulphuric acid. Calculate the amount of alkali neutralized by the sulphuric acid to NaOH.

Free Alkali. Use ten c.c. of the lye and dilute as before, add phenolphthalein as the indicator, and titrate to the discharge of the red color with half-normal sulphuric acid. Calculate to percentage of free sodium hydrate.

Combined Alkali as Sodium Carbonate. To find the combined alkali, express the difference in amounts of sulphuric acid in the two previous titrations in terms of sodium carbonate. This figure divided by the weight of the lye used in each case gives the percent.

Sodium Chloride. Use ten c.c. of the lye and dilute as before, then make slightly acid with nitric acid, and heat to about 60 degrees. Add suffic-

(4) Glycerin.

The method of analysis was as follows:

Specific Trevit. Determined by means of the Westphal balance.

Total Alkali as Sodium Hydrate. Ten c.c. of the waste lye, filtered free from suspended impurities, was placed in a beaker and diluted to about 150 c.c. with distilled water. A few drops of methyl orange was then added and titrated with half-normal sulphuric acid. Calculate the amount of alkali neutralized by the sulphuric acid to NaOH.

Free Alkali. Ten c.c. of the lye was diluted as before, and phenolphthalein as the indicator, and titrated to the disappearance of the red color with half-normal sulphuric acid. Calculate to percentage of free sodium hydrate.

Combined Alkali as Sodium Carbonate. To find the combined alkali, express the difference in amount of sulphuric acid in the two previous titrations in terms of sodium carbonate. This figure plotted by the weight of the lye used in each case gives the percent.

Sodium Chloride. Ten c.c. of the lye was diluted as before, then made slightly acid with nitric acid, and heat to about 60 degrees. Add excess

ient silver nitrate solution to precipitate all the chlorine as silver chloride, and boil until the precipitate has coagulated and the supernatant liquid is clear. Filter on a weighed Gooch crucible by the aid of suction, wash, dry at 105 degrees Centigrade, and weigh. The increase in weight gives the weight of silver chloride from which the percentage of sodium chloride can be calculated.

Glycerine. Place enough of the lye in a 500 c.c. graduated flask, to correspond to about one gram of glycerine, dilute slightly, add silver oxide, allow to stand for ten minutes, and then add a slight excess of lead acetate. Make up to volume, filter, and place 25 c.c. of the clear filtrate into a beaker, then add 40 c.c. of the standard bichromate solution (each c.c. of which has a certain value in glycerine), and 15 c.c. of strong sulphuric acid. Cover the beaker and heat on the water bath for two hours, cool, and titrate back the excess of biohromate with a standard ferrous ammonium sulphate solution. From these results calculate the percentage of glycerine. This reaction may be illustrated by the equation: $C_3H_8O_3$ 3O2 $C_2H_2O_4$ CO_2 $3H_2O$.

Using the above methods, the waste soap liquor analyzed as follows:

Silver analysis is follows:

Using the above method, the route your

Illustrated by the equation: $C_3H_5(OH)_3 + 3OH^- \rightarrow C_3H_5(O^-)_3 + 3H_2O$.

The percentage of glycerine. This reaction may be ill- ammonium sulphate solution. From these results calculate back the excess of thickness with a standard ferrous heat on the water bath for two hours, cool, and titrate c.c. of which has a certain value in glycerine), one 15 c.c. of strong sulphuric acid. Cover the beaker and 40 c.c. of the standard dichromate solution (each 25 c.c. of the clear filtrate into a beaker, then add of lead acetate. Make up to volume, filter, and place to stand for ten minutes, and then add a light excess of glycerine, allow slight slightly, and silver oxide, allow c.c. granulated flask, to correspond to about one gram

Glycerine. Place amounts of the lye in a 500 from which the percentage of sodium chloride can be calculated.

crease in weight gives the weight of silver chloride wash, dry at 105 degrees Centigrade, and weigh. The in- filter on a Gooch crucible by the aid of suction, pitate has completed and the supernatant liquid is clear. chloride as silver chloride, and boil until the precipi-

Specific Gravity	1.073
Total Alkali as NaOH	0.25
Free Alkali as NaOH	0.12
Combined Alkali as Na_2CO_3	0.18
Sodium Chloride	7.27
Glycerine	3.07

The determination of the amount of sulphuric acid necessary to neutralize a given amount of soap lye, and the amount of aluminum sulphate necessary to precipitate the albuminous matter in a given amount of the liquor, was the first step. We used the lye in ten kilogram lots, andthe amount of acid necessary to neutralize this amount was calculated as follows: By means of a pipette we placed 25 c.c. of the lye in a beaker, and added enough half-normal sulphuric acid to neutralize it, using methyl orange as an indicator. It required 3.4 c.c. of the acid to neutralize this amount of the lye, and, since 1 c.c. of half-normal sulphuric acid contains 0.049 gram of $H2S04$, 3.4 c.c. contain 0.1666 gram of H_2S0_4. The weight of 25 c.c. of the lye is 25 x 1.07 or 26.75 grams. Therefore, since 26.75 grams of the lye required 0.1666 grams of sulphuric acid to neutralize it, 10 kilograms, or 10,000 grams require 10,000 / 26.75 x 0.1666 or 62.14 grams of sulphuric acid. The acid used to neutralize the

Specific Gravity	1.072
Total Alkali as Na2O	0.28
Free Alkali as Na2O	0.12
Combined Alkali As Na2O	0.16
Sodium Chloride	7.1%
Glycerine	6.0%

The determination of the amount of sulphuric acid necessary to neutralize a given amount of soap lye, and the amount of aluminum sulphate necessary to precipitate the glycerine matter in a given amount of the liquor, was the first step. We used the lye in the 2liquors lots, and the amount of acid necessary to neutralize this amount was calculated as follows: In making of a pipette we placed 10 c.c. of the lye in a beaker, and added enough half-normal sulphuric acid to neutralize it, using methyl orange as an indicator. It required 3.4 c.c. of the acid to neutralize that amount of the lye, and, since 1 c.c. of half-normal sulphuric acid contains 0.049 gram of H_2SO_4, 3.4 c.c. contain 0.1666 gram of H_2SO_4. The weight of 10 c.c. of the lye is 10 x 1.09 or 10.90 grams. Therefore, since 98.74 grams of the lye required 0.1666 grams of sulphuric acid. The acid used to neutralize the grams required $10{,}000 \times 98.74 \times 0.1666$ or 40.14 grams, or 10,

liquor was that having a specific gravity of 1.84, 1 c.c. of which contains 1.715 grams of H_2SO_4. Therefore, the amount of acid necessary to neutralize ten kilograms of the waste liquor is 62.14 / 1.715 or 34.1 c.c. of the 1.84 acid.

The necessary amount of aluminum sulphate was determined as follows: one hundred c.c. of the lye was placed in a flask, and to it was added, drop by drop, from a burette, a solution of aluminum sulphate, 25 grams per 200 c.c. After the addition of each drop the solution was allowed to settle, and the addition was continued until a precipitate was no longer formed. Ten cubic centimeters were thus required to precipitate all the albuminous matter in 100 c.c. of the soap liquor. This volume was equivalent to 1.25 gram of aluminum sulphate, and since 10 kilograms are equal to 9345 c.c. (10,000 / 1.073), the amount of the sulphate necessary to coagulate the albuminous matter from ten kilograms of liquor is 9345 / 100 x 1.25 or 116.2 grams.

We next placed 10 kilograms ofthe liquor in a kettle and added the necessary amounts of acid and aluminum sulphate as calculated above, and boiled the mixture for a few moments so as to thoroughly mix the contents, and then placed the mass in a galvanized can and allowed it to settle for twenty-four hours. We

FIGURE 1.

repeated this operation eight times, thus having treated 90 kilograms of the waste soap liquor. This amount required 327 c.c. of sulphuric acid having a specific gravity of 1.84, and 2.25 pounds of the aluminum sulphate.

After allowing the albuminous matter to settle, we filtered the liquor through the filter press (see figure 1) at a pressure of 50 pounds per square inch. The filtrate was then run into a Swensen evaporator (see figure 2) and boiled under a vacuum of 27 inches of mercury and a steam pressure of about 20 pounds per square inch. The evaporation was continued until the liquid was reduced as far as possible, that is, the volume was reduced to 26 liters.

The liquid here was somewhat acid, and, as it had to be neutral before continuing the evaporation our next step was to make it so. We determined the acidity in the same manner as already described, and found that 97.05 grams of NaOH were required to neutralize the 26 liters of lye. Upon the addition of this amount of alkali a further precipitation was brought about which we removed by means of the filter press as before.

The liquid was then ready for further evaporation, and this was done in an evaporator smaller

FIGURE 2.

than the one previously used (see figure 3). The vacuum was 25 inches of mercury, the temperature 140 degrees Fahrenheit, and the steam pressure was ten pounds. We noted that as new liquor was added to that already in the evaporator the vacuum went up to al most 27 inches. This was due to the fact that the new cold liquid condensed some of the vapors in the evaporator.

Having treated the 90 kilograms of waste soap liquor in this manner we withdrew the concentrated liquid from the evaporator, and held it until the next lot was ready. The second lot consisted of 110 kilograms, treated exactly as in the first case. When this second lot was withdrawn from the first evaporator and neutralized and filtered,it was added to the first lot and the whole put into the second evaporator (see figure 3). When the liquid was finally taken from this evaporator, after it had been concentrated down as far as possible, it was allowed to cool and settle, whereupon the salt which had been thrown out of solution, settled to the bottom, and was separated from the supernatant liquid by filtration through cloths.

Since we were unable to filter the solution several times during the evaporation as explained in the preceeding pages, because of the too large capacity of the evaporators, it was a very difficult matter to

FIGURE 3.

to separate the salt from the liquid, for the salt was in an excess and the liquid was thick and syrupy, and we could not use a vacuum. The filtrate now had a very sweetish and not unpleasant odor, was thick, and of a yellowish color. Before going farther we had to make this filtrate slightly alkaline, which we did by adding sodium hydrate to the filtrate. The liquid was then ready for purification by distillation in the still and apparatus, which is shown in detail in the blue-print at the beginning of part 11, together with an assembled drawing of the same, and the specifications from which the small model was made. Figure four shows this minature plant, as designed from the aforesaid blue-prints, just before the steam and water connections were made.

At intervals during the above treatment, we took samples of the liquid at various stages of the process, determining the specific gravity of each and the amount of glycerine contained therein. The results were as follows:

Sample.	% Glycerine	Specific Gravity.
At Start.	3.07	1.073
After 1st. filtration	3.14	1.087
After Concentration	63.71	1.364

The operation and description of the appara-

The operation was description of the apparatus

After Condensation	[illegible]	1.744
After Sat. filtration	2.24	1.089
At first.	3.07	2.042
Sample.	% Glycerine	Specific Gravity.

the amount of glycerine contained therein. The results were as follows:

process, determining the specific gravity of each and took samples of the liquid at various stages of the

At intervals during the above treatment, we

lume ever made.

blue-prints, just before the steam and water connec-

this mixture plant, we continue from the elevevats

tion which the small model was made. Figure four shows

an assembled drawing of the same, and the specifications

flow-print at the beginning of part II, together with

full and operation, which is shown in detail in the

then ready for purification by distillation in the

ing boiling hydrate to the filtrate. The liquid was

cate filtrate slightly alkaline, which is due by add-

yellowish color. Before using Parkner we had to make

greenish and not agreement soap, and of a

we could get ride a reading. The filtrate was had a very

in an excess and the liquid was light and spicy, and

to determine the salt from the filtrate. For the salt was

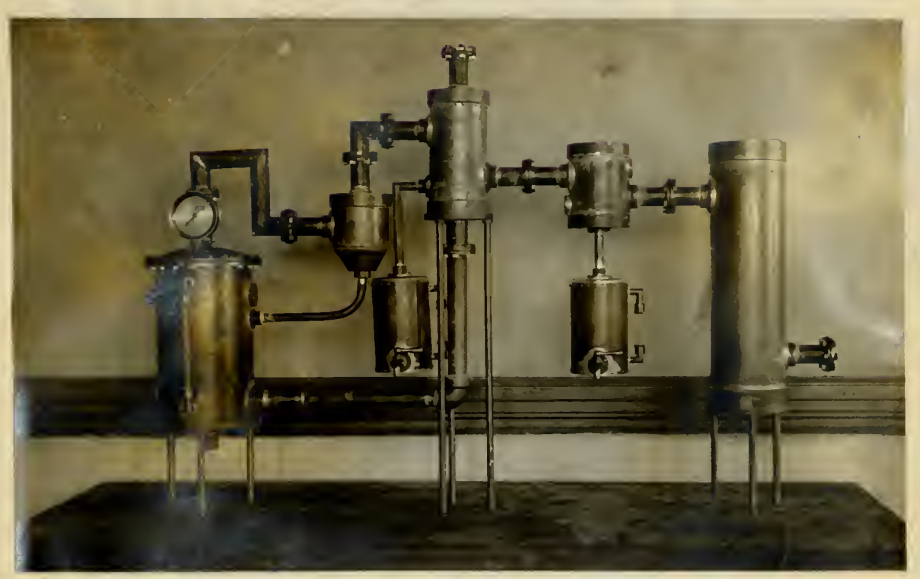


FIGURE 4.

tus which we designed for the purpose of refining the glycerine after leaving the evaporator will now be explained in detail. The letters used refer to the blue prints.

A, is the still proper. It consists of a brass body, at the upper end of which is bolted a brass flanged cover. This cover carries a vacuum gauge and an oil cup in which a thermometer may be placed. The still contains a copper coil, at the lower end of which live steam is admitted and at the upper end of which the steam isexhausted. Into the still at the bottom runs a pipe which terminates in a piece full of small holes, by means of which superheated steam passes.

The liquid from the evaporator was run into the still until it was a little more than half full,as judged from the gauge glass. The steam was then allowed to enter the coil, and as the liquid became heated, the glycerine vapors were evolved. These vapors leave the still at the top, and enter the catch-all, B, while at the same time superheated steam enters the still by means of the perforated pipe at the bottom and helps the vapors to leave the still, and at the same time tending to increase the vacuum by their condensation,

as the superheated steam hits the cooler liquid within the still. As the volume of the liquid in the still decreases more is added so that the still was always about half full. The liquid is added by suction, that is, the vessel containing it is held to the feed pipe near the top of the still and the cock opened. The vacuum within sucks the liquid up into the still.

Those vapors condensing on their way to the catch-all, and in the catch-all, run back to the still by means of the pipe connected from the bottom of the catch-all to the still. Those which do not condense pass out through the top into the superheater C. This superheater is also made of brass. Steam which enters at the top and passes down through vertical copper tubes superheats the glycerine vapors coming from the catch-all, thus preventing them from possibly condensing, and so not passing over into the condenser D. However, the very heaviest vapors do condense in spite of this precaution and run into a receiver, not shown in the blueprints but clearly shown in figure four. The steam which has given up some of its heat to the glycerine vapors passes out at the bottom of the superheater, and enters the still A, at the bottom, after being superheated by means of a Bunsen burner placed at the pipe half way between the still and the superheater.

The glycerine vapors, after being superheated by passing around and amonge the steam pipes of the superheater, pass to D, the condenser proper. This is a brass shell containing a copper coil through which cold water is continually circulating. Here all but a small proportion of the vapors, and those the lightest, are condensed and run into a receiver similiar to the one attached to the superheater, as shown in figure four. The lightest vapors, which do not condense in the condenser, pass to the "sweet-water" condenser E, in which they are condensed by passing around and among vertical copper pipes through which cold water is constantly circulating. The water enters at the bottom and leaves at the top. The condensate is drawn off by the pump which is connected to the lower end of the condenser. If it is desired to save the sweet water, a small receiver can be placed near the condenser in the pipe leading to the pump. The pump is placed at the end of the system to furnish the necessary vacuum, which is increased by the condensation of the superheated steam and vapors, as has been desdribed. The minor details of the apparatus can be readily understood by consulting the drawings.

In practice it has been advisory to place a valve in the pipe leading from the bottom of the catch-

all back to the still. This valve is kept closed until the catch-all contains a certain amount of aondensed vapors, consisting principally of liquid whcih has been carried over mechanically, whereupon the valve is opened and the liquid allowed to run back to the still. This eliminates any traces of salt in the final distillate, for it has been found that this was mechanically carried over in solution though the pipe from the still to the catch-all.

The reason for elways evaporating glycerine in vacuo is due to the fact that when glycerine is heated to its boiling point under atmospheric conditions it decomposes.

When we treated and purified our crude glycerine as above described, we obtained a slight precipitate in the distillate from the receivers. This was due to the passage of some of the crude glycerine from the still to the catch all through the pipe just under discussion. As before said, this could be remedied by placing a valve in the pipe. The precipitate formed in the crude glycerine was probably due to a deterioration of the liquid at some step in the process because of the long intervals which had to elapse between each step. With the pump alone we obtained a vacuum of 25 inches of mercury, when the still was in

operation we obtained a 27 inch vacuum. The temperature at which the distillation was conducted was about 175 degrees Fahrenheit.

When the process of purification was complete, we removed the distillates from the receivers, united them, treated them with sulphuric acid and caustic soda as described in the preceeding pages, mixed it with bone black, and filtered the resulting mixture. We did not carry the purification beyond this point, as the amount of glycerine was too small to warrent further treatment, as the rest of the process is purely mechanical. The glycerine as finally obtained had a specific gravity of 1.239, and contained 90.07 percent of glycerine by analysis.

There remains to be considered the black residuum left in the crude glycerine still. All the organic matter not removed in the preliminary treatment of the lye accumulates in the still and forms this black, viscous residue, which if the distillation be carried too far, becomes so hard as to be removed from the still only with great difficulty. To facilitate its easy handling and the recovery of the considerable quantity of glycerine retained by it, the distillation is checked at that stage beyond which there is danger

of contaminating the distillate with entrained matter from the still. The quantity of glycerine present depends on the concentration and is about 50 per cent. This substance is known as foots.

While yet soft and comparatively fluid, the foots is transferred to a tank and neutralized with oil of vitriol, and then filtered. This product is then concentrated, forming crude glycerine from foots; this is then distilled, and the glycerine thus obtained constitutes the dynamite glycerine of commerce. It is of a pale straw color and requires only subsequent distillation and filtration through bone black to become water-white, chemically pure glycerine of the pharmacopoeia.